

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

SPECIFICATIONS AND CLAIMS OF PATENT APPLICATION

INTEGRATED BIOLOGICAL AND CHEMICAL SENSORS

FIELD OF THE INVENTION

The present invention relates to biological and chemical sensors integrating several physical measurements of target agents.

BACKGROUND OF THE INVENTION

The fast and accurate identification of biological and chemical agents is not only of great interest within the sensor community, but performs a public service by saving lives. The wide dissemination of inexpensive and accurate sensor systems with very low or zero false alarm rates is critical in order to respond to terrorist threats or accidental exposures. False alarms are very costly and could lead to dilatory responses to subsequent real terrorist threats and accidental exposures.

The effectiveness of the first responders depends upon their knowing what hazardous substance has been detected, the concentration of the hazardous substance and the time of the initial exposure. A sensor system which is fast, inexpensive and accurate, and with a low false alarm rate, is critical in both military and civilian applications.

The false alarm rate can be reduced significantly through the use of multiple orthogonal detection methods. Orthogonal methods detect different physical

characteristics of a target agent or substance. For example, optical and gravimetric effects are orthogonal. Gravimetric effects result from mass changes on the resonator, while optical techniques look at the interaction of electromagnetic radiation.

For example, U.S. 5,744,902 to Vig describes detectors using a dual-mode sensor using both a gravimetric and a calorimetric analysis of chemical/biological agents.

However, other than gravimetric and calorimetric, none of the prior art detection systems integrates two or more orthogonal measurements (selected from the following methods: gravimetric, calorimetric, thermal gravimetric, voltage gravimetric, and optical detection methods) into one sensor system, thereby substantially improving the identification of hazardous agents and reducing the false alarm rate.

SUMMARY OF THE INVENTION

The present invention provides an array of piezoelectric resonators, which are used as a "laboratory" for measuring mechanical, physical and chemical effects. The array can be manufactured from a single resonator, or individual resonators can be formed into an array, depending on the application.

The resonators in the array can be arranged into configurations for each test. For gravimetric detection, dual-mode resonators will provide simultaneous calorimetric and gravimetric data, one type from each mode. Resonators with heaters on the surfaces will provide thermal gravimetric data. Further, the heaters can make the resonators "self-cleaning." An optical detector can be used to analyze the optical signal from the surface of a coated resonator; incorporating gold-nano particles into the coating and the electrode of the resonator can enhance the optical signal. Additionally, voltage gravimetric

measurements can be made with an electric field set up between the resonator and an external electrode. Thermal voltage gravimetric measurements can be made by adding an integrated heater on the resonator with an external electrode.

The array of piezoelectric resonators can operate as bulk acoustic wave (BAW), surface acoustic wave (SAW), or Love mode devices.

The integration of gravimetric, calorimetric, thermal gravimetric and optical analytical methods into one sensor system greatly reduces the false alarm rate for detecting chemical and biological agents. For example, after the optical sensor provides data to identify a target agent, the resonators can be used to determine its concentration.

The sensors can be used in buildings and open spaces to monitor terrorist threats for Homeland Security and to identify hazardous waste in environmental applications. They can be used to monitor chemical and biological agents in military and commercial settings. Further, they can be used to detect toxic mold in buildings.

It is an object of the present invention to provide a sensor system capable of detecting a wide variety of chemical and biological agents and concentrations, with an extremely low false alarm rate.

Another object of the present invention is to combine two or more orthogonal detection methods based on gravimetric, calorimetric, thermal gravimetric, voltage gravimetric, and optical measurements.

Still another object of the present invention is to provide a sensor system which is fast and accurate, yet inexpensive.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a top view of an array of bulk acoustic wave (BAW) devices.

Fig. 2 is a cross-sectional side view of the array of the BAW devices illustrated in Fig. 1 taken along line 2-2.

Fig. 3 is a cross-sectional side view of a BAW device, with an external electrode plate.

Fig. 4 is a cross-sectional side view of a BAW device integrated with a fluorescent optical detector system.

Fig. 5 is a representational top view of an array of SAW devices.

Fig. 6 is a representational side view of the array of SAW devices.

Fig. 7 is a top detail view of a single surface acoustic wave (SAW) device.

Fig. 8 is a sectional view of the single SAW device illustrated in Fig. 7 taken along line 8-8.

Fig. 9 is a schematic diagram illustrating the sensor device of the present invention.

Fig. 10 is a representational top view of the sensor device of the present invention, embodied in a hand-held unit.

Fig. 11 is a representational cross-sectional side view of the sensor device illustrated in Fig. 10 taken along line 11-11.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The integrated sensors of the present invention use piezoelectrically-based resonators designed from a piezoelectric crystal such as quartz, lithium niobate, lithium

tantalite, langasite, or Gallium Orthophosphate. The resonators can operate as bulk acoustic wave (BAW), surface acoustic wave (SAW), or Love mode devices. In all cases, the frequency is influenced by material deposited onto the surfaces. When mass is deposited onto the crystal, a change in frequency of the resonator occurs.

The sensors are miniature laboratories capable of measuring mechanical, physical and chemical effects. The sensors described herein can be used for detecting the presence and concentration of chemical and biological agents in a medium of air or liquids. A sensor array is formed from a number of resonators, each a multiple (2, 3 or more) mode piezoelectric resonator, which is energy trapped, having a highly smooth surface relative to the wavelength of the mode. Electrodes formed on each resonator excite the resonator. A coating of nano particles (gold, carbon or another material) can be used to enhance the absorption sites for the target agent (and the resonator's gravimetric response), as well as the optical reflectivity for optical detection. A sensor coating on the resonators will bond, chemically or physically, to certain target agents. Each resonator can have a different sensor coating; some can have no coating at all. The different sensor coatings applied to the resonators in an array are selected so that orthogonal physical properties can be measured, thereby allowing the user to look at the target agent from different directions. A heating element on the resonator controls its temperature and is used to generate data for use in thermal-gravimetric analysis (mass change with heat).

Using conventional means, the medium to be tested is concentrated and then delivered to the surface of the crystal resonators. An excitation circuit causes the multiple modes of the resonators to be excited at the same time so that the mass change and

temperature change can be measured independently, allowing the mass loading to be calculated accurately. A circuit with variable drive levels can be used to detect when the particles on the surface of the resonator become detached. An optical sensor focused on the surface of the resonator can be used to identify the atomic absorption wavelengths of the target agent. The optical sensor can be transmitted, reflected or fluorescent light. A circuit measures the power dissipated in the crystal via the heating element and can be used to determine the heat of reaction between the target agent and the coating on the surface of the resonator (the additional heat generated in the resonator causes a decrease in the heat required to maintain the crystal at a predetermined temperature). A measurement circuit is used to collect the gravimetric, calorimetric, thermal-gravimetric and optical data. An analysis algorithm is used to determine the identify of the target agent. A communications system is used to relay information about the detected agent and its concentration. Finally, an alarm system can be utilized when the target agent and/or its concentration are identified as hazardous.

As shown in Table 1 below, typically the following physical characteristics can be measured:

TABLE 1

<u>PHYSICAL CHARACTERISTICS MEASURED</u>	<u>MEASUREMENT</u>	<u>VARIABLE CONTROL PARAMETER</u>
Gravimetric (mass change)	Frequency of first mode	None
Calorimetric (heat generated)	Frequency of first and second mode	None
Elastic Properties of film	Impedance of first mode	None
Drive Power Effects on Impedance of first mode	Impedance of first mode	Drive Power
Drive Power Effects on Frequency of first mode	Frequency of first mode	Drive Power
Thermal-Gravimetric (mass change with temperature)	Frequency of first mode vs. temperature of resonator	None
Voltage-Gravimetric (mass change with electric field)	Frequency of first mode vs. temperature of resonator	None
Thermal-Voltage Gravimetric (mass change with electric field and temperature)	Frequency of first mode, temperature or resonator, and electric field	Temperature or Voltage

When enough physical characteristics of a target agent are measured, the accuracy of the identification is greatly increased, resulting in zero or near-zero false alarms. In addition, thresholds can be set to permit certain concentrations of target agents to be tolerated, with an alarm sounding only when the concentration reaches an unacceptable

level.

The present invention can be embodied in a bulk acoustic wave (BAW) array **10**, such as the one shown in Fig. 1 and Fig. 2. Formed on a single crystal quartz wafer **11** is an arrangement of BAW resonator plates **12**. The BAW resonator plates **12** can be round, as shown, or can have another shape, such as square or hexagonal. The BAW resonator plates **12** can be arrayed in a 3 x 4 array, as shown, or can be arrayed 2 x 2, 2 x n, 3 x 3, 3 x n, 4 x 4, or 4 x n. The BAW resonator plates **12** have contoured surfaces to improve the short term stability of the resonators by reducing the noise flow.

Depending on its position in the BAW array **10**, each BAW resonator has either a top edge electrode **13** or a top center electrode **14** (on the top side of the crystal quartz wafer **11**), as well as with a bottom edge electrode **15** or a bottom center electrode **16** (on the bottom side of the crystal quartz wafer **11**). The electrodes **13**, **14**, **15**, **16** can be coated with nano particles (e.g., gold) to enhance the absorption of the target agent as well as the optical reflectivity.

Some of the BAW resonator plates **12** will have been coated with a sensor coating **17**, the sensor coatings **17** having been collectively designed to differentially absorb to a specific chemical or biological agent, mass loading the resonator and giving off heat in the reaction. The heat of reaction can be detected by operating the resonator on two modes, using one mode which is temperature compensated (changes very little with temperature) and another which has a large temperature coefficient. For example, a BAW resonator operating on the third overtone C mode, designed with minimum frequency shift over the temperature range can be used with a third overtone B mode over the same temperature

range designed to have a large frequency shift with temperature. A third overtone C mode, designed with minimum frequency shift over a temperature range, could be used with a fundamental C mode, designed to have a higher frequency shift over the same temperature range.

The material used for each sensor coating **17** can be a metal, metallic alloy, polymer, ceramic, carbon, nano-structure, or gold nano-particle. A different coating **17** can be used on each BAW resonator plate **12** in order to detect different target agents.

The BAW sensor array **10** shown in Fig. 1 and Fig. 2 also shows the integrated heater element **18** on two of the BAW resonator plates **17**. The heater element **18** can be used to control the temperature of the BAW resonators. In addition, thermal gravimetric data detectors **19** can be used to monitor the current or voltage through the heater element **18** in order to determine the heat of reaction between the thin film and the target agent; the heat generated in the reaction will decrease the amount of heat required to maintain the resonators at a predetermined temperature. The heater elements **18** can also be used to "self-clean" the resonators and regenerate sensor coatings **17** which have become saturated.

Data collected from the BAW resonator plates **12** includes gravimetric/calorimetric data, thermal-gravimetric data. In addition, information related to the elastic properties of the monolayer can be determined from the loss in the BAW resonators. Further, a circuit with variable drive levels can detect when the particles on the surface become detached.

Fig. 3 shows another embodiment of the present invention. A portion of the crystal quartz wafer **11** has a BAW resonator plate **12**, with a top electrode **20** and a bottom

electrode **21**, which can be coated with nano particles to enhance the absorption of the target agent. The BAW resonator plate **12** has been coated with a sensor coating **17** to bind with a specific chemical or biological agent. A heater element **18** can be used to control the temperature of the BAW resonator plate **12**. An external electrode plate **22** has been arranged to set up an electrical field between the top electrode **20** and the external electrode plate **22**, which provides for the voltage gravimetric measurement of mass loss with applied electric field.

Fig. 4 shows the present invention integrated with an optical detector. A portion of the crystal quartz wafer **11** has a BAW resonator plate **12** with a top electrode **20** and a bottom electrode **21**, which can be coated with nano particles to enhance optical reflectivity. The top electrode **20** on the BAW resonator plate **12** has been coated with a sensor coating **23** which is capable of fluorescing. The optical detector system consists of an optical source **24**, such as an organic light emitting diode (OLED), a separation barrier, or shield **25**, and an optical detector **26**, arranged to detect the fluorescence of biological or chemical agents adsorbed onto the top electrode **20** on the BAW resonator plate **12**. The optical detector system is used to identify the atomic absorption wavelengths of the target agent.

The present invention can also be embodied in a surface acoustic wave (SAW) array **27**, such as the one shown in Figs. 5 through 8. A surface acoustic wave device, such as the one shown, is formed from a quartz crystal designed to support high-frequency acoustics oscillators, which are sensitive to surface effects. The SAW array **27** shown in Fig. 5 and Fig. 6 has a surface acoustic wave (SAW) substrate **28**. Each SAW resonator

has an input electrode **29** and an output electrode **30** coupled to the substrate **28**. A sensor coating **32** can cover a portion of the substrate **28** (as shown) or can cover the electrodes **29**, **30** and the entire upper planar surface of the substrate **28**, so long as the sensor coating **32** material would not corrode the electrodes **29**, **30**.

The SAW resonator can be arrayed in a 3 x 4 SAW array **27**, as shown, or can be arrayed 2 x 2, 2 x n, 3 x 3, 3 x n, 4 x 4, or 4 x n. The electrodes **29**, **30** can be coated with nano particles (e.g., gold) to enhance the absorption of the target agent as well as the optical reflectivity.

Each of the SAW resonators in the SAW array **27** can have a different sensor coating **32** designed to chemically attach to a specific chemical or biological agent, mass loading the resonator and giving off heat in the reaction.

The SAW array **27** shown in Figs. 5 and 6 has integrated heater elements **33** encircling the electrodes **29**, **30** of several of the SAW resonators. The heater elements **33** can be used to control the temperature of the SAW resonators. In addition, the current or voltage through the heater elements **33** can be monitored to determine the heat of reaction, which will decrease the amount of heat required to maintain the resonators at a predetermined temperature. Heat from the heater elements **33** can also be used to "self-clean" the resonators and regenerate sensor coatings **32** which have become saturated.

As shown in Fig. 6, the SAW substrate **28** is thermally insulated by stand-offs **35**.

A single SAW resonator **36** is shown in detail in Fig. 7 and Fig. 8. The input electrode **29** and output electrode **30**, with a sensor coating **32** in between, are disposed on substrate **28**. Electrode wires **31** connect the electrodes **29**, **30** to a power source (not

shown). Similarly, heater element wires **34** connect the heater element **33** to a power source (not shown). In Fig. 8 the electrode contacts **37** and heater contacts **38** can be seen.

Fig. 9 is a schematic diagram illustrating the sensor device of the present invention. The quartz resonator **40** is a resonator formed of a piezoelectric material. As noted supra, the resonator can operate as a bulk acoustic wave (BAW), surface acoustic wave (SAW), or Love mode device. The quartz resonator **40** is excited by electrical signals of varying frequency from the C-mode oscillator **41** and the B-mode or other temperature mode oscillator **42**. A resistance measurement **43** is delivered to the measurement system **44**, as well as data collected from the C-mode oscillator **41** and the temperature mode oscillator **42**. The resonator drive control can cause effects on the frequency and impedance of the C-mode oscillator **41**, which are transmitted to the measurement system **44**. A sensor coating **46** is generally applied to the surface of the quartz resonator **40**. A heater **47** can be attached to or embedded in the surface of the quartz resonator **40**. A heater control circuit **48** controlled by heater microcontroller **49** affects the temperature of the heater **47**, controlling the temperature of the quartz resonator **40**; the temperature measurements are transmitted to measurement system **44**. A gas concentrator **50**, controlled by microcontroller **51**, concentrates the target agent and forces it across the surface of the quartz resonator **40**.

The data from measurement system **44** is delivered to the memory and CPU **52** for analysis and correlation. The results of the analysis are sent to the display **53** for reading by the operator. An alarm sounds if the target agent and/or its concentration are identified

as hazardous. The antenna **55** can be used to transmit the information to a remote location.

The traceable time **56** provides the time (G.M.T.) at which a target agent is being tested. Traceable time, with an accuracy suitable for the application, is critical. In an application where the wind speed could be sixty miles per hour (60 mph), the air is moving at 88 feet per second. Time synchronization within a sensor network must be accurate enough to be usable for predicting the position of a hazardous cloud. Time inaccuracies of 10 seconds in 60 mph wind will lead to errors of 880 feet. Time synchronization using traceable time to 1 millisecond will reduce this error to less than one foot.

The GPS receiver **57** gives the exact location at which the target agent is being tested, detailing the latitude, longitude, and altitude of the test.

Environmental variables **58** provides valuable information relating to such factors as temperature, humidity, wind or air speed, and wind or air direction.

Table 2, below, shows the characteristics measured by the present invention, the measurement means, and the resulting measurements.

TABLE 2

<u>CHARACTERISTIC MEASURED</u>	<u>MEASUREMENT MEANS</u>	<u>MEASUREMENT</u>
Gravimetric	From C-mode oscillator	Frequency or voltage
Temperature	From B-Mode or other temperature mode oscillator	Frequency or voltage → temperature
Resistance (loss)	Resonator peak width	Slope of peak at frequency
Drive	Current of crystal	Current or voltage
Heater current	Current	Current
Time	Clock	Date and time
Location	GPS Receiver	Latitude, longitude, altitude
Temperature	Thermometer	Degrees
Humidity	Barometer	Barometric pressure
Air speed and direction	Anemometer	Velocity and direction

Figs. 10 and 11 show a typical sensor device **60** of the present invention embodied in a hand-held configuration. Disposed within a conventional rectangular housing **61** is the sensor array **62**, which can be comprised of piezoelectric-based resonators designed from quartz, lithium, niobate, lithium tantalite, langasite, Gallium Orthophosphate, or any piezoelectric crystal. The resonators (described *supra* in more detail) in the sensor array **62** can operate as bulk acoustic wave (BAW), surface acoustic wave (SAW), or Love mode devices. The sensor array **62** is connected electronically to the sensor array **63**, which

generally consists of several circuits, including an excitation circuit for each of the multiple modes; a circuit with variable drive levels; a circuit to provide heat; a circuit used to measure the power dissipated in the crystal via the heater and further used to determine the heat of reaction between the target agent and the coating on the resonator surface; a measurement circuit used to collect data, incurring resonant frequencies and magnitudes of impedance over a frequency range; and an optical sensor. The sensor array electronics **62** are connected to microcontrollers **64, 65, 66, 67** and to the memory **68, 69**, which together correlate and characterize the data, comparing, for instance, the sensed frequencies with reference frequencies. A battery **70** provides power for operation of the hand-held embodiment **60**. An antenna **71** can be used to transmit data to a remote location.

As shown in Fig. 11, an air-borne target agent is pulled through filter **72** by air pump **73**, and is then concentrated by concentrator **74**. The target agent has been forced across the sensor array **62**, using a piezoelectric fan or MEMS-based fan. Then, a pumping system **75** removes it from the hand-held embodiment **60**, forcing it out through exit filter **76**. The results of the analysis of the data related to the target agent are shown on the display screen **77**.

Although the description contains much specificity, these details should not be construed as limiting the scope of the invention, but merely providing illustrations of some of the presently preferred embodiments of this invention. Thus the scope of the invention should be determined by the appended claims and their legal equivalents, rather than by the examples given.